

## Supplementary Information

### A stable and high-voltage resistant inorganic/polymer double-layer electrolyte for LiCoO<sub>2</sub> based all-solid-state Li batteries

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#### Experimental section

##### Fabricate LCO cathode :

800 mg LCO, 100 mg Super P and 100 mg PVDF were mixed and stirred 24 h in NMP to form a homogenized solution at 25 °C. The cathode was readily fabricated by spreading LCO slurry on carbon-coated Al surface using a doctor blade, then stored in a vacuum oven at 110 °C for 12 h and separated into small circles with a diameter of 15 mm.

##### Produce a LiPON layer on LCO surface :

The cathode was cleaned by high-purity Ar gas, then transferred to the vacuum chamber. When the background pressure of the chamber reached  $9.9 \times 10^{-4}$  Pa, high-purity N<sub>2</sub> gas at a flowing rate of 50 sccm was introduced to maintain the working pressure (1.0 Pa). Simultaneously, RF power supply with 120 W was applied to deposit the LiPON buffer layer.

##### Preparation of solid polymer electrolyte :

2000 mg PEO and 406 mg LiTFSI ( $\text{Li}^+$ : EO = 1:32) were dissolved in acetonitrile and a homogeneous solution was formed by stirring for 24 h at room temperature. Then, 900 mg succinonitrile was added into the homogeneous solution and still stirred for 12 h to form SPE solution. Finally, 2 mL SPE solution was cast onto the LiPON-coated LCO surface and dried in a vacuum oven at 60 °C for 12 h so as to remove the acetonitrile solvent.

## Supplementary Figures

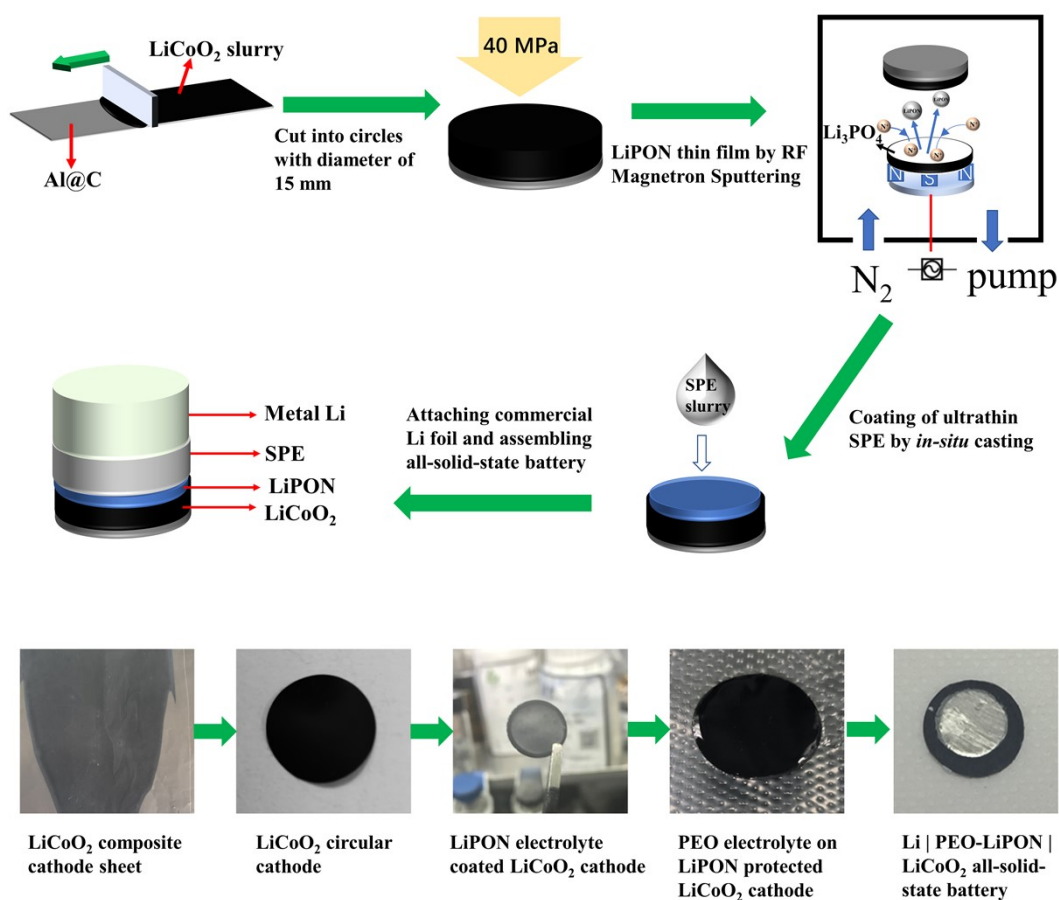


Figure S1 Schematic drawing of the experimental procedure and the corresponding optical image snapped at each stage.

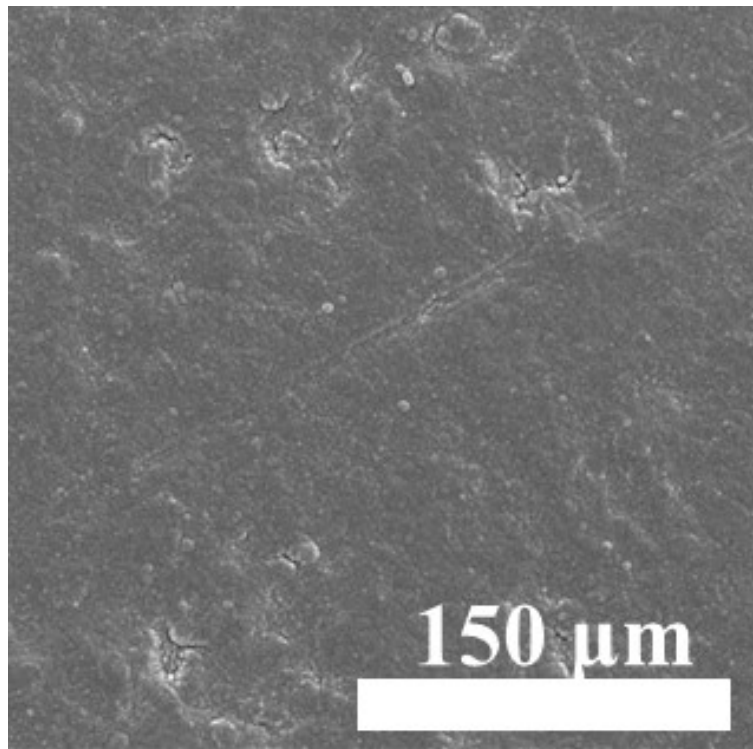


Figure S2 Top-view SEM image of LiPON

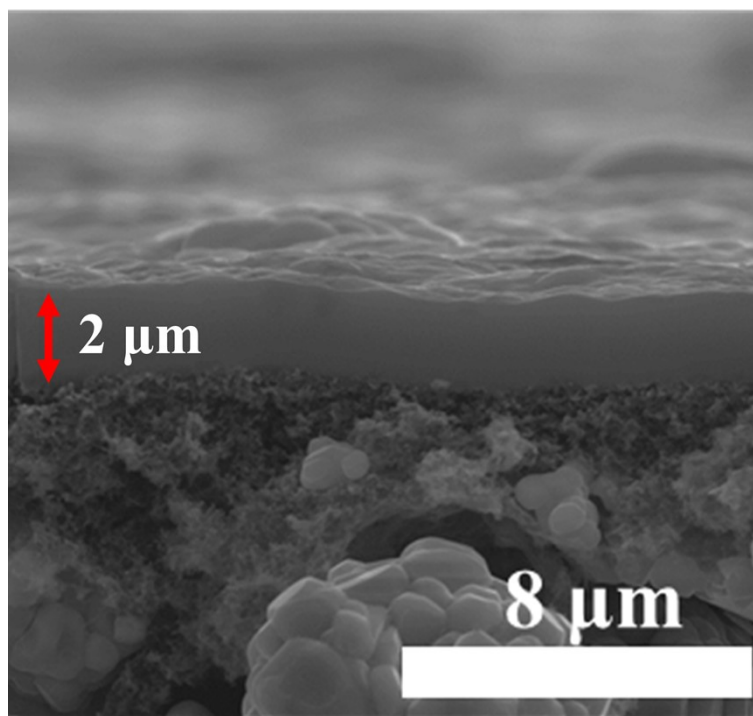


Figure S3 The zoom-in cross-sectional SEM image of 2 μm thick LiPON-coated LCO cathode.

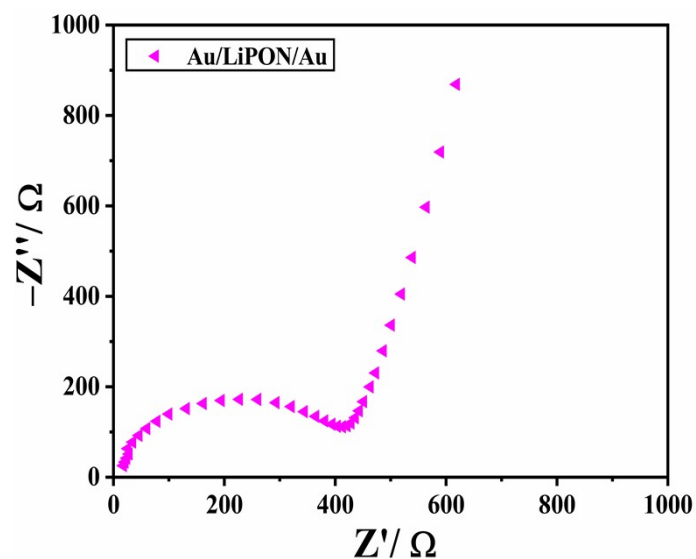


Figure S4 EIS measurements of Au|LiPON|Au.

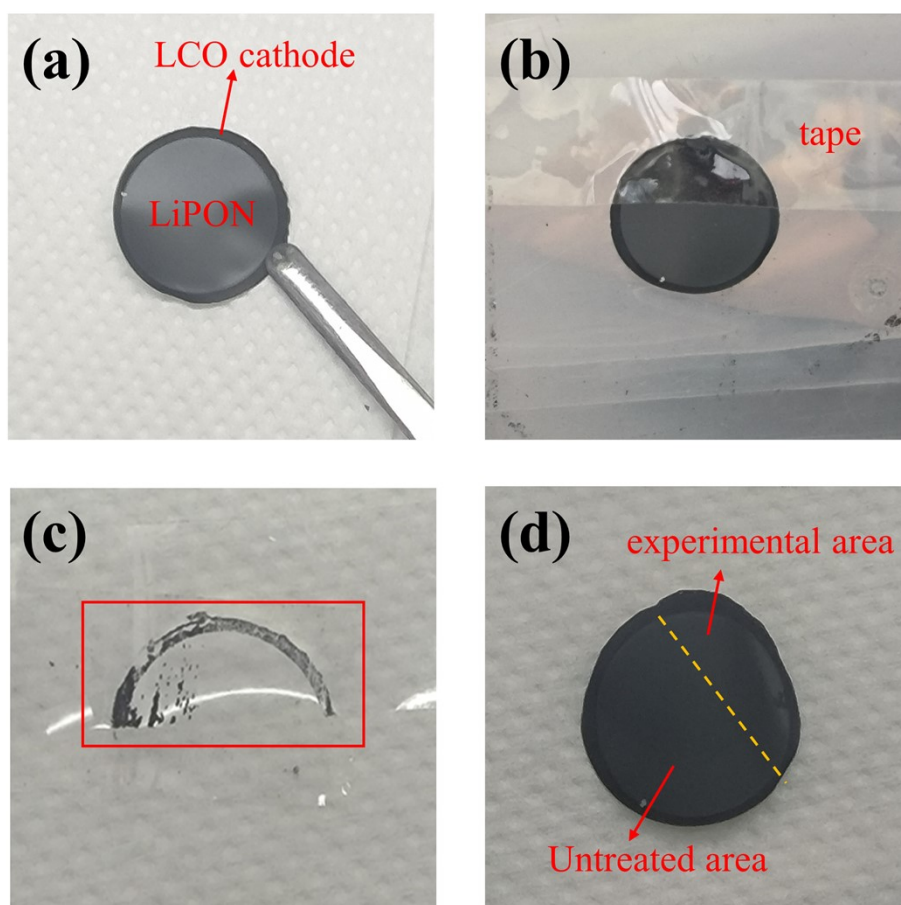


Figure S5 Optical photograph of (a) LiPON-coated LCO; (b) the half of LiPON-coated LCO is fixed with tape; (c) the peeled off tape; (d) the difference between experimental area and untreated area.

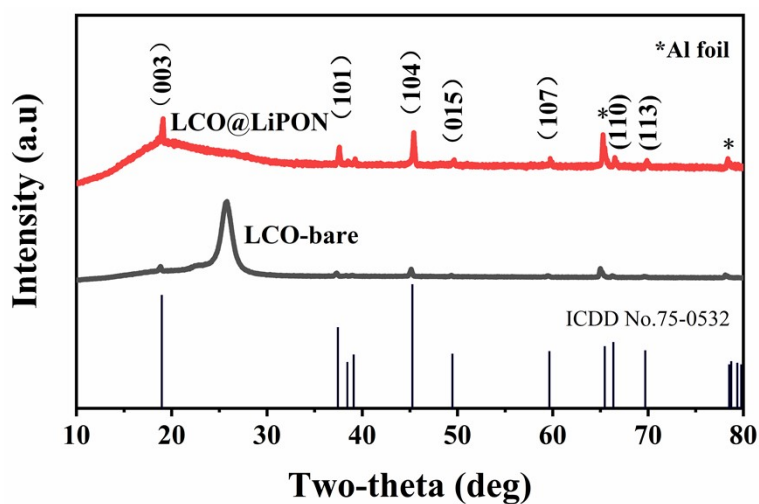


Figure S6 XRD patterns of LCO and LiPON-coated LCO.

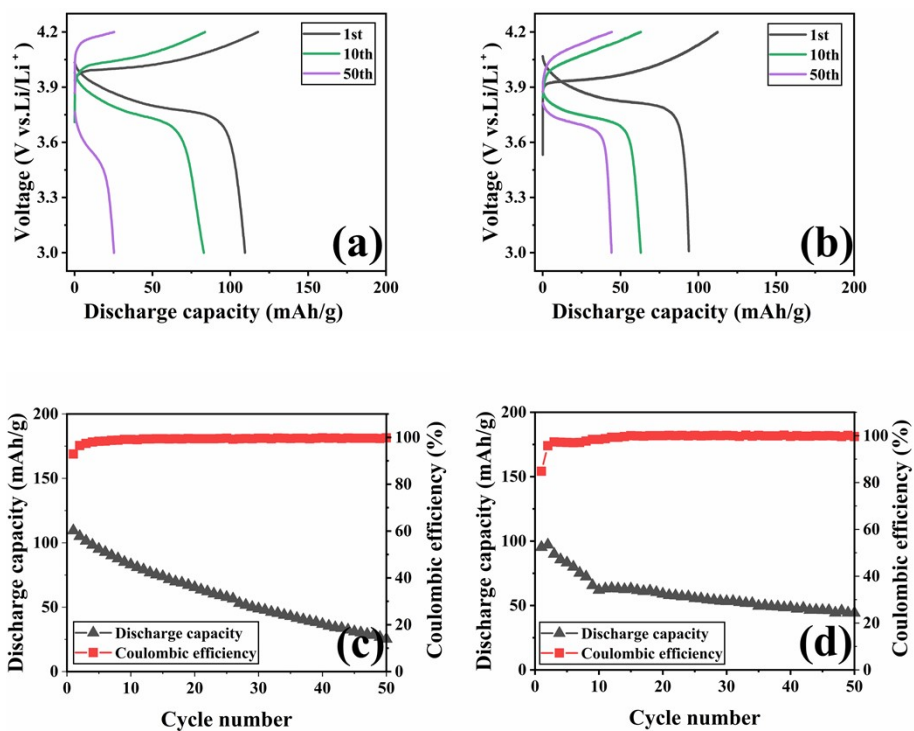


Figure S7 The charge and discharge curves at the 1st, 10th and 100th cycle under the cut-off voltage of 4.2 V (a) LCO|SPE50|Li and (b) LCO|SPE100|Li; the cyclic performances of (c) LCO|SPE50|Li and (d) LCO|SPE100|Li.

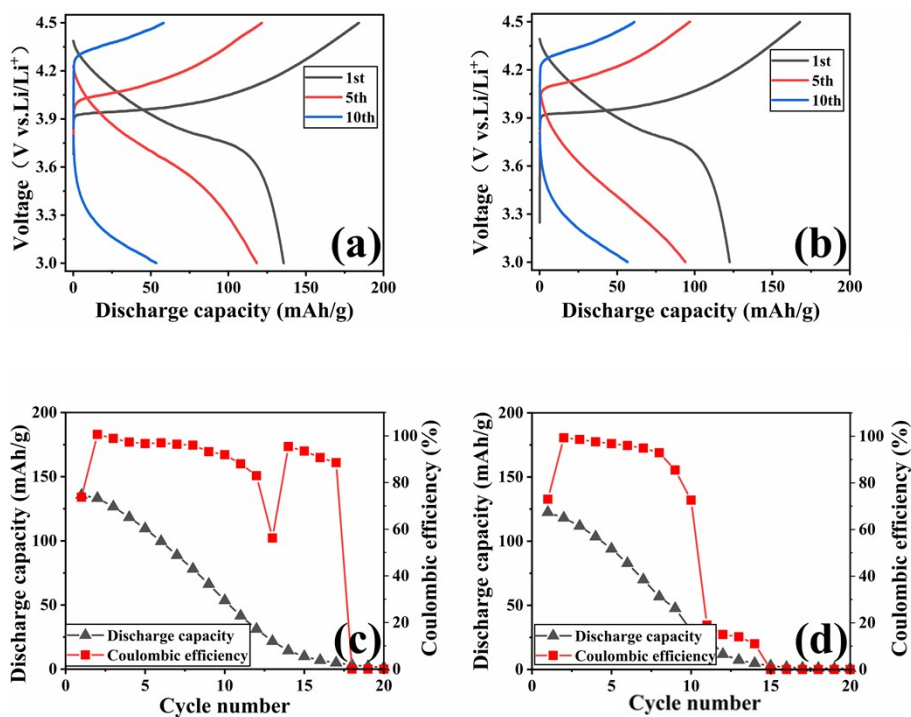


Figure S8 The charge and discharge curves at the 1st, 10th and 100th cycle under the cut-off voltage of 4.5 V (a) LCO|SPE50|Li and (b) LCO|SPE100|Li; the cyclic performances of (c) LCO|SPE50|Li and (d) LCO|SPE100|Li.

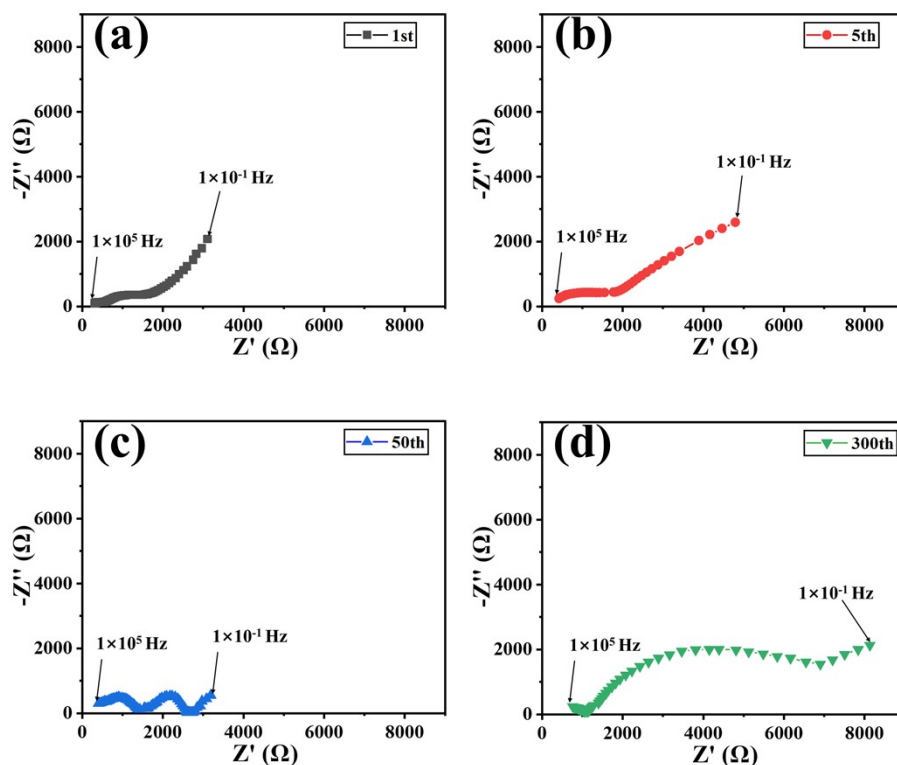


Figure S9 EIS data of LCO|LiPON-SPE|Li cell at (a) 1st; (b) 5th; (c) 50th; (d)300th.

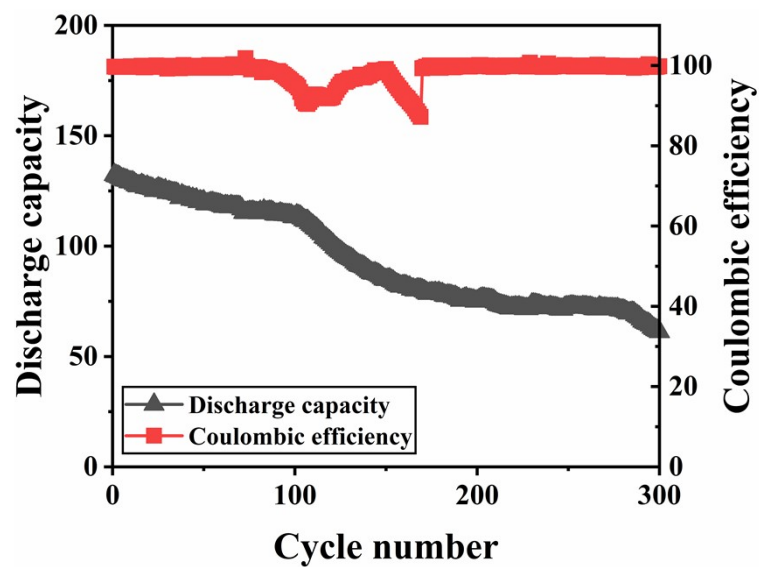


Figure S10 The long cyclic performance of LCO|LiPON-SPE|Li.